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ABSTRACT

This unit is one of a group of units written to fit the Certificate of Sixth Year Studies (CSYS) chemistry course, but it could be used in most Sixth Form courses. These materials are designed for use in a group decision-making format with each of three groups representing a different manufacturing process which produces vinyl chloride. The unit contains three parts: (1) presentation of different manufacturing processes in separate groups; (2) combining the groups; and (3) further activities. Materials include: teacher packet (background, guidelines and answers); general student background information; information packets for each manufacturing group (with guidelines and considerations); combined group guidelines; and suggestions for further activities. Experience and interaction among students during decision making should help them understand that decisions in the chemical industry are multidisciplinary. (DH)

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THE VINYL CHLORIDE PROBLEM

This unit is one of a group of units written to fit the Certificate of Sixth Year Studies Chemistry course but could certainly find a place in most Sixth Form courses.

The series has been written by a group of teachers, college lecturers, university lecturers and industrialists.

It has been supported financially by the Education Appeal Fund of the Royal Society of Chemistry and the Education for the Industrial Society Group of the Scottish Curriculum Development Service and has received the approval of the Chemistry Panel of the Scottish Examination Board.

It is hoped that this will be used in an interactive way to give pupils the experience of making decisions for themselves on the basis of their chemical knowledge and the knowledge of other disciplines, so that they may truly see that the decisions of chemical industry are of necessity - multi disciplinary.

We realise that this unit will not be perfect and we would welcome helpful criticism so that later editions can be improved.

Dr. A.H. Johnstone
General Editor.

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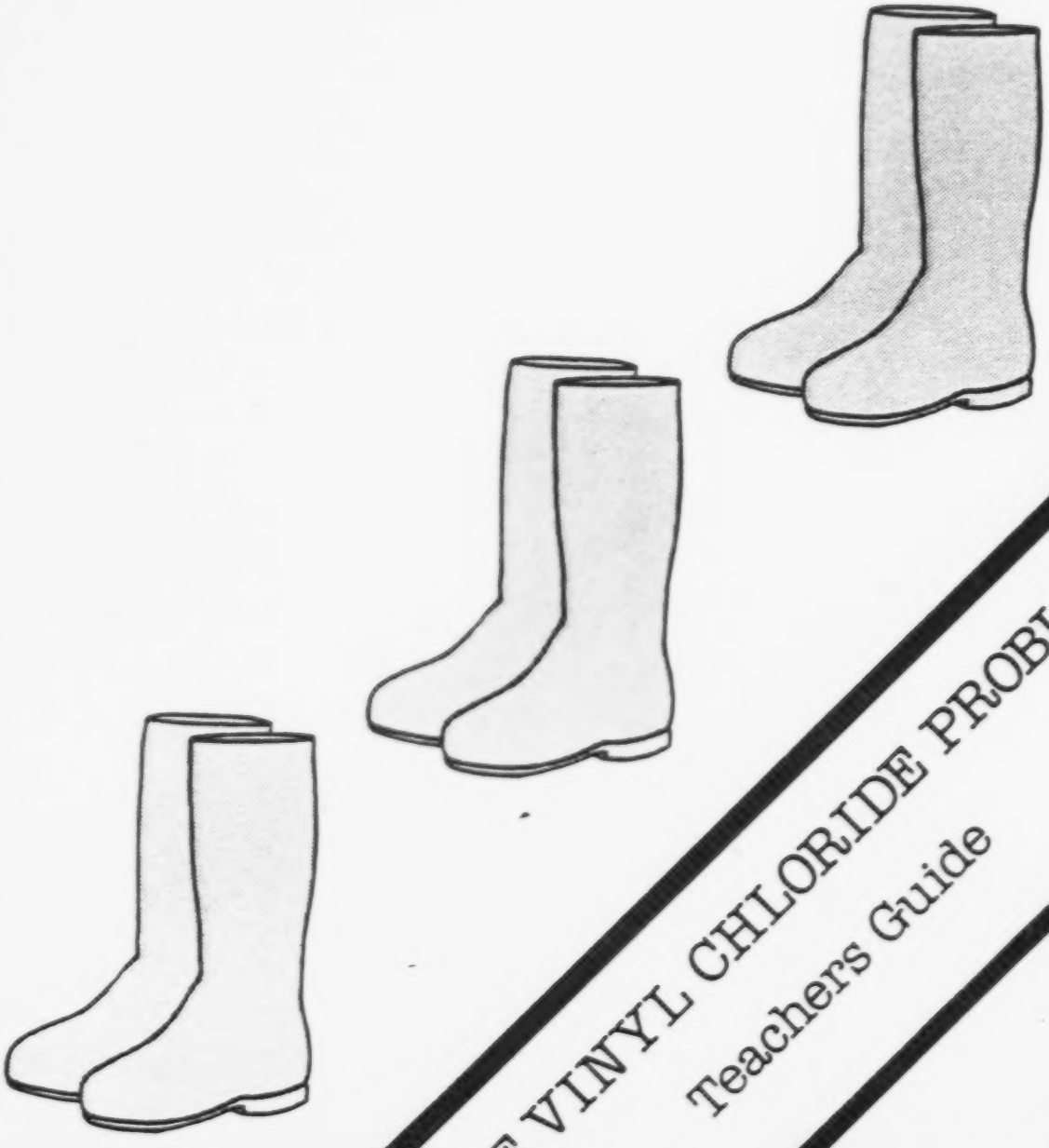


THE VINYL CHLORIDE PROBLEM

Teachers Guide

THE VINYL CHLORIDE PROBLEM

TEACHERS GUIDE

Format: Group Decision Making

Time: Two double periods or one complete afternoon (This may be extended if desired).

Number of pupils: For this exercise the pupils should be divided into three groups. If the numbers dictate two groups only, then only two of the three routes in Part 1 should be attempted.

Instructions: All pupils should be issued with the introduction and should work through it. On completion, they will discuss in class the questions raised before being divided into groups for the issue of Part I.

They work through Part 1 using the data given to find the cost of making 1 tonne of VCM. They then come together and discuss their results after being issued with Part II.

They may finish at this point or take the problem further using Part III.

Objectives:

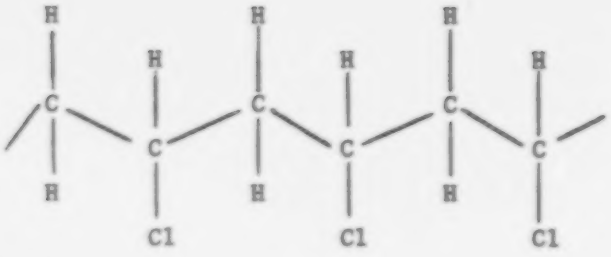
1. To use chemical equations to calculate combining masses.
2. To assess the cost of making a chemical.
3. To assess factors other than costs e.g. hazards.
4. To show there is rarely a best way of making a chemical for which there is a high demand.

Uses of PVC

Engineering and Building Materials	Clothing	Food, Entertainment and Leisure
Weatherproof coating for link fencing	Raincoats Wellingtons	Garden hose-pipes Gramophone records
Car underseal	Footwear	Chocolate box and biscuit tin liners
Water pipes, drains, gulleys and roans	Plastic baby pants	Sweetie jars Food wrapping
Cable & wire insulation		Paddling pools
Insulation tape		Swimming pool liners
Lead-acid battery - cell separating grids		Audio, video & data storage tapes
Washable vinyl covered wallpaper		
Blister packs for tools		
Floor coverings, tiles, shower curtains		

Raw Materials Salt, Petroleum, Coke, Water

Structure



OR

$-CH_2-\ CHCl-CH_2-\ CHCl-CH_2-\ CHCl-$

PART 1

The class should divide into groups to discuss and cost the following methods of making vinyl chloride.

Group 1

Costing for the route -

$$\text{calcium dicarbide} \xrightarrow{H_2O} \text{ethyne} \xrightarrow[HgCl_2]{HCl} \text{vinyl chloride}$$

Group 2

Costing for the route -

$$\text{oil(naphtha)} \xrightarrow{\text{crack}} \text{ethyne} \xrightarrow[HgCl_2]{HCl} \text{vinyl chloride}$$

Group 3

Costing for the route -

$$\text{naphtha} \xrightarrow{\text{crack}} \text{ethene} \xrightarrow{Cl_2} \text{1,2 - dichloroethane} \xrightarrow{\text{crack}} \text{vinyl chloride + HCl}$$

Teachers' Notes for Group 1,

Step 1 $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + HC{\equiv}CH$

$\underbrace{40+24}_{64}$ $\underbrace{40+34}_{74}$ 26

1 tonne C_2H_2 = $\frac{1}{26}$ tonne mole

requires $\frac{1}{26} \times 64 \times \frac{100}{80}$ tonne CaC_2

costing £$\frac{1}{26} \times 64 \times \frac{100}{80} \times 200$ = £615

also produced is $\frac{74}{26} \times \frac{100}{80}$ tonne $Ca(OH)_2$

which can sell for £$\frac{74}{26} \times \frac{100}{80} \times 2$ = £7

Net cost of ethyne £615 - £7 = £608
(approx. pence are rounded off)

Steps 1 and 2 could combine here as Step 2 is common to both groups except that cost of ethyne is different.

Step 2 $\underbrace{C_2H_2}_{26} + \underbrace{HCl}_{36.5} \xrightarrow{HgCl_2} \underbrace{CH_2CHCl}_{62.5}$

£608 $\times \frac{1}{62.5} \times 26$ + 55 $\times \frac{1}{62.5} \times 36.5$

£253 + £32 = £285

£285 $\times \frac{100}{85}$ For 85% conversion = £335

$HgCl_2$ cost $\frac{2}{100}$ x £335 = £7

Total cost of 1 tonne vinyl chloride = £342

PART 1

Teachers' Notes for Group 2

Step 1

1 tonne naphtha produces 0.25 tonne ethyne

1 tonne ethyne requires $\frac{1}{0.25}$ tonne naphtha

costing £$\frac{1}{0.25}$ x 160 = £640

energy running costs = £270

Total cost of 1 tonne of ethyne = £910

Step 2

$C_2H_2 + HCl \xrightarrow{HgCl_2} CH_2{=}CHCl$

26 36 62.5

£910 x $\frac{1}{62.5}$ x 26 + £55 x $\frac{1}{62.5}$ x 36

£379 + £32 = £411

£411 x $\frac{100}{85}$ for 85% conversion = £484

add $HgCl_2$ cost of £7 per tonne VCM = £ 7

Total cost of 1 tonne vinyl chloride = £491

Teachers' Notes for Group 3

Step 1 1 tonne of naphtha produces 0.5 tonne ethene

1 tonne ethene requires 2 tonnes naphtha

costing = £320

energy and running costs = £270

Total cost of 1 tonne of ethene = £590

Step 2 $CH_2CH_2 + Cl_2 \xrightarrow{FeCl_3} ClCH_2 - CH_2Cl$

28 71 99

1 tonne 1, 2-dichloroethane is $\frac{1}{99}$ tonne mol which requires:

$CH_2{=}CH_2$ + Cl_2

$\frac{1}{99}$ x 28 $\frac{1}{99}$ x 71 tonne

cost £590 x $\frac{28}{99}$ + £$\frac{71}{99}$ x 90

= £167 + £65 £232 x $\frac{100}{98}$ = £237

add 2% for catalyst cost = £242

Total cost 1 tonne dichloroethane = £242

Step 3 $ClCH_2{-}CH_2Cl \xrightarrow{heat} ClCH{=}CH_2 + HCl$

99 62.5

Cost of 1 tonne 1, 2-dichloroethane £242

This gives theoretical yield of $\frac{62.5}{99}$ tonnes VCM

Actual yield of $\frac{0.95 \times 62.5}{99}$ = 0.6 tonne VCM

Cost per tonne VCM = $\frac{£242}{0.6}$ = £403

Add energy and running costs of £280

Gives a total cost of £683 per tonne.

PART 2

Teachers' Notes on Combining Groups 1, 2 and 3.

All groups join to discuss the use of HCl, formed in the cracking of 1, 2-dichloroethane to make more vinyl chloride from ethyne.

The groups should see that 'waste' HCl obtained by the cracking of 1, 2-dichloroethane can be utilised.

Group 3 have costed the process:

$$CH_2{=}CH_2 + Cl_2 \longrightarrow ClCH_2CH_2Cl \longrightarrow \underbrace{CH_2{=}CHCl}_{62.5} + \underbrace{HCl}_{36.5}$$

Every tonne of vinyl chloride produces $\frac{1}{62.5}$ x 36.5 tonnes of hydrogen chloride, which will require

$\frac{1}{62.5}$ x 26 tonne of ethyne, costing either

From dicarbide

$$£\frac{1}{62.5} \times 26 \times 609 \times \frac{100}{85} = £298$$

or

From cracking

$$£\frac{1}{62.5} \times 26 \times 910 \times \frac{100}{85} = £445$$

The above costs allow for the 85% yield of the reaction but not the cost of catalyst (2%) which must be added (£6 & £9) giving £304(dicarbide) and £454 (cracking).

Thus we can get 2 tonnes of vinyl chloride for the cost of 1 tonne by group 3 (£683) plus £304 or £454 giving 2 tonnes for £987 (carbide) or £1137 (cracking).
Thus costs per tonne are £493.5 or £568.5.

PART 3

Teachers' Notes on Taking it Further.

Pupils are invited to think of converting HCl from the cracking of 1, 2-dichloroethane to chlorine. This chlorine can therefore be recycled using air as the oxidising agent.

$$2HCl + \tfrac{1}{2}O_2 \xrightarrow{Cu^{2+}} H_2O + Cl_2;\ \Delta H = -92.3\ kJ\ mol^{-1}$$

On the basis of the direct method, encourage the pupils to consider the process;

$$HCl + \tfrac{1}{2}O_2 + CH_2{=}CH_2 \qquad CH_2{=}CHCl + H_2O$$

derived in the steps suggested in the "Taking it Further" data sheet;

$$2HCl + \tfrac{1}{2}O_2 \longrightarrow H_2O + Cl_2 \quad \ldots\ldots(i)$$

$$Cl_2 + CH_2{=}CH_2 \longrightarrow ClCH_2\text{-}CH_2Cl \quad \ldots\ldots(ii)$$

Add (i) and (ii);

$$2HCl + \tfrac{1}{2}O_2 + CH_2{=}CH_2 \longrightarrow ClCH_2\text{-}CH_2Cl + H_2O \quad \ldots\ldots(iii)$$

Dichloroethane cracking;

$$2ClCH_2\text{-}CH_2Cl \longrightarrow 2CH_2{=}CHCl + 2HCl \quad \ldots\ldots(iv)$$

Add two times (iii) and (iv);

$$\underbrace{2HCl}_{2 \times 36.5} + O_2 + \underbrace{2CH_2{=}CH_2}_{2 \times 28} \longrightarrow \underbrace{2CH_2{=}CHCl}_{2 \times 62.5} + 2H_2O$$

Counting the cost

1 tonne of vinyl chloride is $\frac{1}{62.5}$ x 36.5 tonne HCl

costing £$\frac{1}{62.5}$ x 28 x 590 + £$\frac{1}{62.5}$ x 36.5 x 55

= £296 x $\frac{100}{60}$

= £493

Add 2% for catalyst (£10)

Add energy cost (£100)

Total cost £603

THE VINYL CHLORIDE PROBLEM

Pupils Introduction

AIM

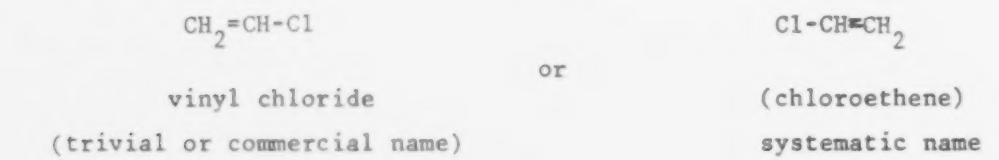
Given that a small organic molecule can be manufactured in several ways using different starting materials, to show that the manufacturer's choice of methods of making such a substance is influenced not only by chemical considerations but also by costs of starting compounds, expense of the process, and hazards of the process and by-products.

INTRODUCTION

The organic compound chloroethene, which is a sweet smelling gas boiling at -14°C (259K), has been known for well over one hundred years. For most of this time it was a compound of little importance and so its preparation was limited to laboratories, but since 1918 interest in the commercial possibilities of this material has led to its large scale manufacture.

Let us first think of the reason for requiring this compound in such large quantities.

In the chemical industry chloroethene is known as VCM. These initials give a clue to its importance; they stand for vinyl chloride monomer. Vinyl chloride is the original name of the compound; chloroethene is the systematic name.



vinyl chloride (trivial or commercial name) — (chloroethene) systematic name

Most useful compounds discovered years ago are better known in commerce by their trivial names; another example is acetylene (rather than ethyne). These names often do not give any clue to the structure of the compound, whereas the systematic names do.

But the word to note particularly is monomer - where there's a monomer there's a polymer - that is to say if anything is called a monomer, this implies the existence of a polymer, and it is the polymer, polyvinyl chloride, PVC, which is important. Only a few professional chemists have a deep interest in VCM for its own sake, but we all, chemists and non-chemists alike, are making use of PVC.

(Throughout the rest of this unit, we shall use VCM rather than referring to vinyl chloride or chloroethene).

THINGS TO DO

First for each pupil:

1. Make a list of as many common, everyday articles as you can think of that are made of PVC.

2. Write down the elements present in PVC and try to write down the names of the raw materials from which these elements might be obtained.

3. Draw a section of a PVC molecule showing three monomer units. When you have done this come together as a group to discuss your findings.

PVC is clearly of major industrial importance. We are going to outline how it might be made by various processes and then try to decide on the important factors which would help us to choose the best method.

To do this the class will divide into groups. Each group will consider a particular method of making VCM and work out the cost of making one tonne (10^3Kg) by that process; when this has been done the class will meet again to discuss findings and the advantages and difficulties of each method.

PART 1

GROUP 1

HOW TO MAKE VCM

In considering the manufacture of any compound the chemist starts by noting the elements which are present in the molecule. The starting materials chosen must also contain these elements. VCM contains the elements carbon, hydrogen and chlorine. The most common source of chlorine is sodium chloride; carbon and hydrogen occur in combination as hydrocarbons. Although the most important source of hydrocarbons in the world today is oil, an alternative source is calcium dicarbide, from which ethyne (or acetylene) may be obtained.

$$CaC_2 + 2H_2O \longrightarrow C_2H_2 + Ca(OH)_2$$

Since ethyne contains the same number of carbon atoms as VCM, this may prove a useful route to that compound.

It is not difficult for a chemist to devise several synthetic routes to the same compound; but on an industrial scale, cost is one of the main factors in deciding which route to choose.

Your group will calculate the cost of manufacturing VCM from ethyne obtained from calcium dicarbide. The other groups will perform a similar calculation using other starting materials. Each group will assess other factors such as hazards involved and present its findings to the rest of the class. The class as a whole will then try to reach a decision on which (if any) of the methods considered can be deemed the best method.

Procedure. You have to assess the cost of manufacturing one tonne (i.e. 10^3Kg) of VCM, starting from calcium dicarbide. The process takes place in two steps; the calculation for the first of these has been carried out for you. Work through this, noting the procedure used, then go on to do the calculation for the second stage. Use the 1980 prices given on your data sheet (page 3).

The production of VCM from calcium dicarbide takes place in two steps:

Step 1: $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

Step 2: $C_2H_2 + HCl \xrightarrow[\text{(Catalyst)}]{HgCl_2} H_2C{=}CHCl$

The cost of calcium dicarbide is £200 tonne^{-1}

We must first calculate the cost of producing 1 tonne of ethyne.

Write the balanced equation and calculate formula weights:

$$\underset{64}{CaC_2} + 2H_2O \longrightarrow \underset{74}{Ca(OH)_2} + \underset{26}{C_2H_2}$$

Since 1 tonne ethyne is equivalent to $\frac{1}{26}$ tonne mole, we will require $\frac{64}{26}$ tonnes calcium dicarbide

Hence the cost of 1 tonne ethyne is $\frac{64}{26} \times 200$ i.e. £492

At first sight, therefore, the cost of ethyne is £492 tonne^{-1}.

However in real life we must take additional factors into account.

ONE VERY IMPORTANT FACTOR which we have not yet considered is that organic reactions rarely produce a yield of 100%.

In this reaction the yield of ethyne is found to be only 80%.

What effect will this factor have on the cost? There are two possibilities:

Either the cost will be £492 $\times \frac{80}{100}$ i.e. £393 tonne^{-1}

or the cost will be £492 $\times \frac{100}{80}$ i.e. £615 tonne^{-1}

Decide which of these is the correct one.

Which did you decide was the correct answer?
We are having to use more starting material to make one tonne of ethyne, so the correct answer is £615 tonne^{-1}.

A second important factor is: Can we sell any other product of the reaction? In this case the other product is calcium hydroxide. You probably know that this is used by farmers (for what purpose?)

If the cost of calcium hydroxide is £2 tonne^{-1}, what effect will this have on the price of ethyne?

For every tonne of ethyne produced there will be

$$\frac{100}{80} \times \frac{74}{26} \text{ tonnes calcium hydroxide}$$

Hence the cost will be $2 \times \frac{100}{80} \times \frac{74}{26}$ i.e. £7

Do we add this figure to the cost already found, or subtract it from the cost? Since we are selling this quantity of material it will have the effect of making the ethyne LESS expensive than it would have been, hence

Net cost of 1 tonne ethyne = £615 - £7
= £608

What we have done is to use the data from Table 1 below to calculate the cost of 1 tonne ethyne.

TABLE 1

Equation: $CaC_2 + 2H_2O \longrightarrow Ca(OH)_2 + C_2H_2$

Cost of calcium dicarbide: £200 $tonne^{-1}$

Selling price of calcium hydroxide: £2 $tonne^{-1}$

Yield of ethyne: 80%.

Now use the information given in Table 2 below to calculate the cost of 1 tonne VCM.

TABLE 2

Equation: $C_2H_2 + HCl \xrightarrow[\text{Catalyst}]{HgCl_2} H_2C=CHCl$

Cost of HCl: £55 $tonne^{-1}$

Cost of C_2H_2: £608 $tonne^{-1}$

Yield of VCM: 85%

Cost of "loss" of traces of catalyst: £7 for every tonne of VCM formed.

Having worked out the cost of VCM, appoint a spokesman for your group to present your findings to the other participants. (You may wish to prepare an overlay for the overhead projector; if not, a blackboard presentation will be necessary).

Give some consideration to the following points:-

(1) Are any of the compounds involved hazardous to human beings? If so, what extra precautions will be necessary?

(2) Are any of the compounds involved particularly corrosive? (Remember that industrial scale reactions are not carried out in glassware!).

(3) Are there any waste products? If so will there be any waste disposal problems?

(4) Are there any other factors we might have taken into consideration when costing the process?

Having done this, and made any notes you think necessary to assist you to answer any questions, you should now join the members of the other groups to present your findings and compare them with theirs. What you must ultimately decide is whether or not one method of making VCM is superior to the other two.

PART 1

GROUP 2

HOW TO MAKE VCM

In considering the manufacture of any compound, the chemist starts by noting the elements which are present in the molecule. The starting materials chosen must also contain these elements.

VCM contains the elements carbon, hydrogen and chlorine. The most common source of chlorine is sodium chloride; carbon and hydrogen occur in combination as hydrocarbons.

The most important source of hydrocarbons is oil; but only a very tiny proportion of the molecules in crude oil contain the same number of carbon atoms as VCM. A way must therefore be found of altering the size of larger molecules in oil to reduce them to a chain length of two carbon atoms. This process (as you already know) is called cracking.

It is not difficult for a chemist to devise several synthetic routes to the same compound; but on an industrial scale, cost is one of the main factors in deciding which route to choose.

Your group will calculate the cost of manufacturing VCM from naphtha, a fraction obtained from the distillation of crude oil. The other groups will perform a similar calculation using either a different route or different starting material. Each group will assess other factors such as hazards involved, and present its findings to the rest of the class. The class as a whole will then try to reach a decision on which (if any) of the methods considered can be deemed the best method.

Procedure. You have to assess the cost of manufacturing one tonne (10^3Kg) of VCM starting from naphtha, with ethyne as an intermediate compound. The process takes place in 2 steps; the calculation for the first of these has been carried out for you. Work through this, noting the procedure used, then go on to do the calculation for the second stage. Use the 1980 prices given on your data sheet.

The production of VCM from naphtha via ethyne takes place in two steps:

Step 1 Naphtha (Mainly a mixture of alkanes) $\xrightarrow{\text{heat}}$ complex mixture of alkenes and alkynes from which ethyne may be separated by distillation

Step 2 $C_2H_2 + HCl \xrightarrow[\text{Catalyst}]{HgCl_2} H_2C{=}CHCl$

TABLE 1

Cost of naphtha (b.p. range 35-200°C)	: £160 tonne^{-1}
Cost of energy for cracking and separation:	£270 tonne^{-1} ethyne produced.
Yield of ethyne :	0.25 tonne per tonne naphtha.

From Table 1 we see that one tonne naphtha yields only 0.25 tonnes ethyne. Hence cost of ethyne is 4 x 160 i.e. £640 tonne^{-1}.

We have not taken into account the cost of energy, which we are told is £270 tonne^{-1} ethyne produced. This must be <u>added</u> to the previous figure i.e.

Total cost of ethyne is 640 + 270 i.e. £910 tonne^{-1}.

Note that the yield of ethyne is only 25%. In general, organic reactions give yields which are less than 100% and allowance must be made for this.

We must also look carefully to see if we can <u>sell</u> any unwanted by-products, which in this case are the other products of the cracking process. The sale of these has been taken into account in arriving at the figure of £270 tonne^{-1} ethyne energy cost.

Now use the information in Table 2 to calculate the cost of one tonne VCM.

TABLE 2

Equation:	$C_2H_2 + HCl \xrightarrow[\text{catalyst}]{HgCl_2} H_2C{=}CHCl$
Cost of HCl:	£55 tonne^{-1}
Cost of C_2H_2:	£910 tonne^{-1}
Yield of VCM:	85%
Cost of "loss" of traces of catalyst:	£7 for every tonne of VCM formed.

Having worked out the cost of VCM, appoint a spokesman for your group to present your findings to the other participants. (You may wish to prepare an overlay for the overhead projector; if not, a blackboard presentation will be necessary).

Give some consideration to the following points:-

(1) Are any of the compounds involved hazardous to human beings? If so, what extra precautions will be necessary?

(2) Are any of the compounds involved particularly corrosive? (Remember that industrial-scale reactions are not carried out in glassware!)

(3) Are there any waste products? If so, will there be any waste disposal problems?

(4) Are there any other factors we might have to take into consideration when costing the process?

Having done this, and made any notes you think necessary to assist you to answer any questions, you should now join the members of the other groups to present your findings and compare them with theirs. What you must ultimately decide is whether or not one method of making VCM is superior to the other two.

PART 1

GROUP 3

HOW TO MAKE VCM

In considering the manufacture of any compound, the chemist starts by noting the elements which are present in the molecule. The starting materials chosen must also contain these elements.

VCM contains the elements carbon, hydrogen and chlorine. The most common source of chlorine is sodium chloride; carbon and hydrogen occur in combination as hydrocarbons.

The most important source of hydrocarbons is oil; but only a very small proportion of the molecules in crude oil contain the same number of carbon atoms as VCM. A way must therefore be found of altering the size of larger molecules in oil to reduce them to a chain length of two carbon atoms. This process (as you already know) is called cracking.

It is not difficult for a chemist to devise several synthetic routes to the same compound; but on an industrial scale cost is one of the main factors in deciding which route to choose.

Your group will calculate the cost of manufacturing VCM from naphtha, a fraction obtained from the distillation of crude oil. The other groups will perform a similar calculation using either a different route or a different starting material. Each group will assess other factors such as hazards involved, and present its findings to the rest of the class. The class as a whole will then try to reach a decision on which (if any) of the methods considered can be deemed the best method.

Procedure. You have to assess the cost of manufacturing one tonne (10^3Kg) of VCM starting from naphtha, with ethene as an intermediate product. The process takes place in three steps; the calculation for the first of these has been carried out for you. Work through this, noting the procedure used, then go on to do the calculations for the second and third steps. Use the 1980 prices given on your data sheet.

The production of VCM from naphtha via ethene takes place in three steps.

Step 1: Naphtha (mainly a mixture of alkanes) $\xrightarrow{\text{heat}}$ complex mixture of alkenes and alkynes from which ethene may be separated by distillation.

Step 2: $CH_2{=}CH_2 + Cl_2 \xrightarrow[\text{Catalyst}]{FeCl_3} ClCH_2CH_2Cl$ [ΔH negative]

(98% yield)

Step 3: $ClCH_2CH_2Cl \xrightarrow{\text{heat}} ClCH{=}CH_2 + HCl$ [ΔH positive]

TABLE 1

Cost of naphtha (b.p. range 35-200°C) : £160 tonne^{-1}
Cost of energy for cracking and separation : £270 tonne^{-1} ethene produced
Yield of ethene : 0.5 tonne per tonne naphtha

From Table 1 we see that one tonne naphtha yields 0.5 tonnes ethene.

Hence cost of ethene is 2 x 160 i.e. £320 tonne^{-1}

We have not taken into account the cost of energy which we are told is £270 tonne^{-1} ethene produced. This must be <u>added</u> to the previous figure i.e.

Total cost of ethene is £320 + £270 i.e. £590 tonne^{-1}.

Now use the information in Tables 2 and 3 to calculate the cost of 1 tonne VCM.

TABLE 2

Equation: $C_2H_4 + Cl_2 \xrightarrow[\text{Catalyst}]{FeCl_3} ClCH_2CH_2Cl$
Cost of ethene: calculated in Step 1.
Yield of 1:2 dichloroethane: 98%
Catalyst loss: allow 2% of the total raw material cost.

TABLE 3

Cost of 1:2 dichloroethane: calculated in Step 2
Energy cost of VCM: £280 tonne^{-1}

When you have completed this task proceed to page3.

Having worked out the cost of VCM, appoint a spokesman for your group to present your findings to the other participants. (You may wish to prepare an overlay for the overhead projector; if not, a blackboard presentation will be necessary).

Give some consideration to the following points:-

(1) Are any of the compounds involved hazardous to human beings? If so, what extra precautions will be necessary?.

(2) Are any of the compounds involved particularly corrosive? (Remember that industrial-scale reactions are not carried out in glassware!)

(3) Are there any waste products? If so, will there be any waste disposal problems?

(4) Are there any other factors we might have to take into consideration when costing the process?

Having done this, and made any notes you think necessary to assist you to answer any questions, you should now join the members of the other groups to present your findings and compare them with theirs. What you must ultimately decide is whether or not one method of making VCM is superior to the other two.

PART 2

FURTHER INFORMATION FOR ALL GROUPS COMBINED

Groups 1 and 2 have made VCM by the addition of HCl (cheap) to ethyne (expensive) by a simple process which needs a modest amount of cooling and some account to be taken of the corrosive nature of the HCl used.

Group 3 has made VCM by a more complex, 2 stage process from chlorine (more expensive than HCl) and ethene (cheaper than ethyne). Did any of you in Group 3 notice you were throwing away half the chlorine you started with during the cracking of 1,2 dichloroethane to VCM?

Ask the spokesman from either Group 1 or 2 if there is a way of converting this loss of HCl into a gain of VCM.

Things to do.

As a combined group adjust the cost of VCM using additional ethyne (cost from Groups 1 and 2) to mop up the by-product HCl (from Group 3) to form vinyl chloride.

PART 3

TAKING IT FURTHER - IF TIME PERMITS

"Is this the whole story?" you may well ask. We now know which is the cheapest method - from ethyne, from ethene, or from both (the so called balanced process). Making various allowances for the availability or various raw materials, transport costs, demands for by-products etc. we could now decide in any particular case. The answer is, "No this is not the whole story". The industrial chemist is never satisfied to rest on his laurels but is always looking for improvements and it is quite possible that in the 21st century PVC will not be made by any of the current processes. Indeed by then it is possible that PVC may no longer be of commercial importance.

We have seen that the ethene process, which works with chlorine rather than hydrogen chloride, uses only half the available chlorine to make VCM and the by-product hydrogen chloride cannot be used with ethene. What a pity that ethene cannot be converted to VCM using hydrogen chloride: that way we would convert all our chlorine using the cheap process.

Things to do

Discuss the possibility of converting hydrogen chloride to chlorine. How can this be achieved? If the reaction is to be introduced into a competitive industrial process, expensive laboratory reagents like potassium permanganate (potassium manganate (VII) are out. We are looking for something which is really cheap - indeed if it costs nothing so much the better.

If you have the right answer then you have "rediscovered" the Deacon process, an obsolete method of manufacturing chlorine. The Deacon process declined because the chlorine obtained was mixed with a large excess of nitrogen. Potential buyers of chlorine want pure chlorine and not nitrogen containing a small percentage of chlorine. However, if the chlorine is manufactured where it is to be used, that is in the reaction vessel along with ethene, then the excess nitrogen is not a serious drawback.

(i) Write an equation for the reaction converting hydrogen chloride to chlorine. A catalyst is used in the process; copper (II) or iron (III) salts - this will add about 2% of the final cost of VCM to the total cost per tonne of VCM.

(ii) Write a balanced equation for the addition reaction of chlorine to ethene. Adjust the numbers of molecules involved in this equation so that there are the same number of molecules of chlorine on the LHS of this as there are on the ~~RHS of the previous one.~~

(iii) Add the two equations together cancelling any items that appear on both sides.

(iv) Write a balanced equation for the cracking of dichloroethane to give chloroethene and by a similar procedure to the above add it to your last equation to get a net equation for the overall process - that for the oxychlorination of ethene.

(v) Calculate the cost of making a tonne of VCM by this method (ethene £590 per tonne, hydrogen chloride £55 per tonne and including £100 for energy per tonne VCM). Assume the yield is only 60% for the overall reaction. Other factors which have not been discussed so far are corrosion and the use of dangerous materials on a large scale.

Corrosion

Since large scale industrial processes are carried out in steel rather than glass, apparatus corrosion can be a serious problem. Hydrogen chloride and chlorine are both corrosive and this fact must be added to costs of building the chemical reactors

Processes 1 and 2, from ethyne, have only one step involving corrosive HCl.

Process 3 has 2 steps, the addition of chlorine and the separation of hydrogen chloride from 1,2-dichloroethane. This plant will be more expensive than the ethyne process.

The extra processes devised from processes 1-3 are simpler in plant requirements, being one step processes, but to offset this are hard to get to work efficiently.

Hazards

Hydrogen chloride and chlorine are obvious hazards, but the chemical industry has sufficient experience with these substances to use them safely.

Other hazards have appeared during the history of the development of the manufacture of VCM and its use. These hazards were not anticipated because of lack of knowledge.

The first unexpected hazard is mercury (II) chloride. Mercury compounds are well known as poisons, used for controlling plant diseases such as cabbage club root and also for controlling the attack of fungi on stored seed. However, in the ethyne process mercury (II) chloride is used as a catalyst and not much is lost during the process. People thought that provided the wastes from this process were well diluted/

/diluted there was no hazard. However Hg^{2+} is a poison which has been shown to be biologically converted, near industrial waste outfalls, to alkyl mercury compounds e.g. $(CH_3)_2Hg$, which are absorbed by marine organisms - fish and shellfish. These are then transmitted to people if they eat contaminated fish, and this causes irreversible brain damage.

An additional cost factor has therefore to be added to the ethyne based processes to allow for the expense of Hg^{2+} removal from effluent.

Vinyl chloride, thirty years or so after the start of its large-scale manufacture, was found to be responsible for liver damage, bone damage and a rare form of liver cancer. This led industries manufacturing vinyl chloride to reduce the concentrations of vinyl chloride in the working atmosphere of chemical plants from 1000 parts per million to 5 parts per million, requiring another cost factor to be added to the cost of manufacture of vinyl chloride by any route.

Setting up the plant

In the above calculations we have not considered the construction of the plant to manufacture VCM. Purchase of the site, building of the plant, security, road construction, etc. will all have to be taken into consideration in determining the cost of the VCM produced. If we had done this today it would have made our calculations very much more complex; but in the real-life situation we could not have neglected it.

Final Points

You might like to discuss just how much the risk of making a chemical can be justified by the usefulness of the end product. As with most real life situations, there is no right answer.

PRODUCTION TEAM

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